PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-269388
(43)Date of publication of application : 19.10.1993

(51)Int.Cl. B01J 35/04
B01D 53/36
B28B 11/04
C04B 41/85

(21)Application number : 04-351934
(22)Date of filing : 09.12.1992

(71)Applicant : NGK INSULATORS LTD
(72)Inventor : KOTANI WATARU
HAMAGUCHI KUNIKAZU
KASAI YOSHIYUKI

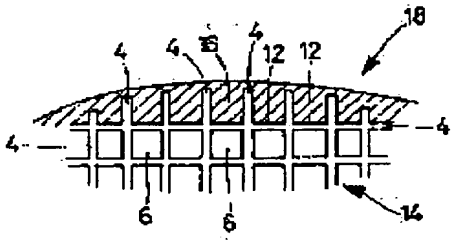
(30)Priority
Priority number : 404 4010 Priority date : 30.01.1992 Priority country : JP

(54) CERAMIC HONEYCOMB STRUCTURE, ITS PRODUCTION AND COAT MATERIAL THEREFOR

(57)Abstract:

PURPOSE: To reinforce a honeycomb structure, to improve the peeling resistance of a shell layer for the reinforcement, to improve the resistance to heat and thermal shock, to facilitate the production and to ameliorate the practicality.

CONSTITUTION: Many cells 6 are surrounded by a partition wall 4 extending in the axial direction and separated from one another, the cell positioned on the outermost side of the periphery is not provided with the partition wall between itself and the outside, and a recessed groove 12 opened to the outside and extending in the axial direction is formed in a ceramic honeycomb main body 14. At least the recessed grooves 12 at the periphery of the main body 14 are filled with a coat material to form an outer shell layer 16 constituting the outer surface.



LEGAL STATUS

[Date of request for examination]	22.09.1994
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	2613729
[Date of registration]	27.02.1997
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] What is located in the outermost part of the periphery section among the cels of a large number which are prolonged in shaft orientations, and which were surrounded by the septum and divided mutually by not having a septum between the exteriors The ceramic honeycomb structure object equipped with the ceramic honeycomb body which forms the concave which carries out opening outside and is prolonged in shaft orientations, and the outer shell layer of the periphery section of this ceramic honeycomb body which is filled up with a concave at least and forms an outside surface.
[Claim 2] The ceramic honeycomb structure object according to claim 1 with which this cordierite exists in this outer shell layer in the shape of a particle while having the main crystal phase which said outer shell layer becomes from cordierite.
[Claim 3] The ceramic honeycomb structure object according to claim 1 with which said outer shell layer consists of a cordierite particle and/or ceramic fiber, and an amorphous oxide matrix that exists among them.
[Claim 4] The ceramic honeycomb structure object according to claim 3 said whose amorphous oxide matrix is a matrix formed with colloidal silica or a colloidal alumina.
[Claim 5] AISO static reinforcement is 3 kg/cm2. Ceramic honeycomb structure object according to claim 2 700 degrees C or more and whose generating temperature of a crack thermal shock resistance is 800 degrees C or more above.
[Claim 6] The ceramic honeycomb structure object according to claim 3 with which said ceramic fiber consists of an amorphous mullite or amorphous silica alumina.
[Claim 7] What is located in the outermost part of the periphery section among the cels of a large number which are prolonged in shaft orientations, and which were surrounded by the septum and divided mutually by not having a septum between the exteriors The process for which the ceramic honeycomb body which forms the concave which carries out opening outside and is prolonged in shaft orientations is prepared, The process for which the coat material which contains a cordierite particle and/or ceramic fiber, and a colloid oxide as a principal component is prepared, Apply this coat material to the peripheral face of said ceramic honeycomb body, and it is filled up with the concave which exists in the peripheral face of this ceramic honeycomb body. The manufacturing method of the ceramic honeycomb structure object characterized by including the process which forms the outer shell layer of predetermined thickness, and the process which makes the outer shell layer formed in the peripheral face of this ceramic honeycomb body dry or calcinate, and makes this ceramic honeycomb object fix this outer shell layer.
[Claim 8] The manufacturing method of the ceramic honeycomb structure object according to claim 7 said colloid oxide is colloidal silica or a colloidal alumina, and is made to blend at a rate of 3 - 35 weight section by solid content conversion to the 100 weight sections of said cordierite particle and/or ceramic fiber.
[Claim 9] Coat material for forming the outer shell layer of a ceramic honeycomb structure object which contains a cordierite particle and/or ceramic fiber, and a colloid oxide as a principal component.
[Claim 10] Coat material according to claim 9 said colloid oxide is colloidal silica or a colloidal alumina, and is made to blend at a rate of 3 - 35 weight section by solid content conversion to the

100 weight sections of said cordierite particle and/or ceramic fiber.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to a ceramic honeycomb structure object and its manufacturing method list at the coat material for it, reinforces a ceramic honeycomb structure object effectively, and makes the manufacture easy, and relates to the technique which can raise the practicality advantageously.
[0002]
[Background of the Invention] In recent years, strengthening of automobile exhaust regulation is considered in relation to the air pollution control. And although the catalytic converter which makes support the ceramic honeycomb structure object which has the through tube (cel) of a large number surround by the septum formed in one of extrusion molding is use for the emission gas purification of current and an automobile , examination of improvement in the so-called warm up property which raises the catalytic activity from the early stages of a start up is perform by make it easy to make small the heat capacity of this honeycomb structure object , and to get warm as a policy which raises the purification effectiveness further .
[0003] And the cure whose thing (reduction in bulk density) for which it is made light it is required, therefore make it thin, the thickness, i.e., the honeycomb rib thickness, of a septum of a cel, or makes porosity high will be taken, without changing the geometric surface area of a honeycomb structure object, in order to make small the heat capacity of such a ceramic honeycomb structure object. Moreover, in an automobile, although there is an increment in catalyst area, i.e., adoption of the cure to which the volume of a honeycomb structure object is made to increase, as an approach with easy No. 1 of raising purification effectiveness, if modification of loading area is difficult and a honeycomb structure object is connected with a serial for the increment in the catalyst volume, an exhaust back pressure becomes large and is inherent in problems, such as leading to the fall of engine power. For this reason, there is no rise of such an exhaust back pressure, in order to make catalyst area increase, rib thickness which divides the cel of a honeycomb structure object mutually is made thin, the hole density of a honeycomb structure object is raised, and it is considered to be the good plan which raises purification effectiveness to make the honeycomb catalyst volume increase.
[0004] The three way component catalyst processing which particulate discharge was also made into the problem besides the same problem of discharge of NOx, CO, and HC as the usual gasoline engine vehicle, on the other hand, performed purification with a particle removal filter (DPF) to the particulate in the emission gas purification of a diesel-power-plant vehicle, and used the honeycomb structure object for NOx is considered. It **, and from the place whose object cars of a diesel-power-plant vehicle are a motor coach, a truck, etc., displacement is large, since exhaust gas concentration is also deep, the large-scale honeycomb structure object is needed for performing purification actuation like ****, and the large-sized thing to which an outer diameter amounts also to 300mm is needed.
[0005] By the way, the fall of the mechanical strength of a honeycomb structure object is a thing, therefore each direction of the formation of a thin wall of the honeycomb septum in a honeycomb structure object confirmed for the cure against exhaust gas toughening of regulations like the above and the reduction in bulk density by the increment in porosity is making various kinds of problems cause in a honeycomb structure object. The formation of a thin wall of a honeycomb septum is very

difficult on industrial engineering, and the extrusion rate balance of clay water mixture changes with extrusion parts of the dice for extrusion molding on the occasion of the extrusion molding. For example, to eye others The piece (crack) of a cel **** defect or an outer wall arises into a periphery part, or since [of the honeycomb structure object (generation form) acquired] the reinforcement of the extrusion generation type article is low, crushing and deformation of a cel by self-weight are mainly caused, and the problem to which dimensional accuracy worsens is inherent. Moreover, since a mechanical strength is weak and it is easy to be destroyed in the first stage applied to each application of a honeycomb structure object as compared with other parts, in order for the cel defective part which exists in such a honeycomb structure object to secure the reinforcement of a thin wall-ized honeycomb structure object, it is necessary to remove such a cel defect. And without being constituted by the normal cel and generating a crack etc., if it puts in another way, also in the structure which a thin wall-ized honeycomb structure object does not include for cel ****** with such a weak mechanical strength where the outer wall was fabricated in one, AISO static reinforcement (periphery grasping reinforcement) does not fill reinforcement required in the case of canning of such the structure, but a certain periphery reinforcement is needed.

[0006] Moreover, when enlarging this honeycomb structure object and obtaining large-sized support and DPF, it also sets. If the appearance is set to about 300mm, it will become difficult to fabricate a uniform outer wall in one. Moreover, the generated type article of a honeycomb structure object The shape retaining property falls, and crushing and deformation are caused with a self-weight, therefore dimensional accuracy is bad, and the part where mechanical strength is low is made to generate further from the place where reinforcement is very weak by the periphery section.

[0007] the purpose of reinforcement of the bottom of this situation, and a honeycomb structure object -- with, it is shown clearly that it is shown clearly with the ingredient which comes to mix a silicic acid zirconium to a specific silicate that the periphery section of a honeycomb structure object is covered, and water-repellent periphery reinforcement refractories are prepared in the peripheral face of a honeycomb structure object at JP,50-48858,U, and the approach of applying a cover coat to a peripheral-wall front face is clarified further at JP,51-44713,B at JP,53-133860,U. On the other hand , by fill up the passage near the periphery section of honeycomb support with a predetermined ceramic ingredient in JP,56-129042,A also in an applicant for this patent , the structure which raise the reinforcement of the periphery section be proposed , and the enveloping layer with which a difference with the dimension make into the dressed size and purpose at the peripheral wall of a honeycomb structure object be compensate in JP,63-144836,U be prepared , and the structure which be made to perform the reinforcement be proposed .

[0008] However, the processing technique over the periphery section of the honeycomb structure object of these former As for neither, the reinforcement effectiveness is enough, or thermal resistance is bad, and are inherent in the problem of generating exfoliation and the crack of an enveloping layer. Further All of the reinforcement demanded as honeycomb catalyst support for automobile exhaust purification, thermal resistance, a heat-resistant impact property, and dependability are not satisfied.

[0009]

[Problem(s) to be Solved] The place which this invention makes this situation a background, succeeds in it in here, and is made into the technical problem is to raise the practicality remarkably, making the peeling resistance of an outer shell layer established for the reinforcement improve, and improving thermal resistance and thermal shock resistance, and using manufacture of still such a honeycomb structure object as easy while aiming at effective reinforcement of a honeycomb structure object.

[0010]

[Means for Solution] What is located in the outermost part of the periphery section among the cels of a large number which were surrounded by the septum and divided mutually prolonged in shaft orientations for this technical-problem solution this invention and by not having a septum between the exteriors Carry out opening outside and let the ceramic honeycomb structure object equipped with the ceramic honeycomb body which forms the concave prolonged in shaft orientations, and the outer shell layer of the periphery section of this ceramic honeycomb body which is filled up with a concave at least and forms an outside surface be the summary.

[0011] In addition, in this ceramic honeycomb structure object, the outer shell layer has advantageously the main crystal layer which consists of cordierite, and such cordierite exists in an outer shell layer in the shape of a particle. Moreover, this outer shell layer consists of a cordierite particle and/or ceramic fiber, and an amorphous oxide matrix that exists among them advantageously. And the amorphous oxide matrix which constitutes an outer shell layer is a matrix formed with colloidal silica or a colloidal alumina advantageously. Furthermore, as ceramic fiber, what consists of an amorphous mullite or amorphous silica alumina advantageously will be used. And for such a ceramic honeycomb structure object of a configuration, generally, the AISO static reinforcement is 3 kg/cm2. It is formed so that it may have the property that it is above, and the thermal shock resistance is 700 degrees C or more, and the generating temperature of a crack is 800 degrees C or more further.
[0012] Moreover, this invention that the ceramic honeycomb structure object which has the writing **** description should be manufactured (a) what is located in the outermost part of the periphery section among the cels of a large number which are prolonged in shaft orientations, and which were surrounded by the septum and divided mutually by not having a septum between the exteriors The process for which the ceramic honeycomb body which forms the concave which carries out opening outside and is prolonged in shaft orientations is prepared, (b) A cordierite particle and/or ceramic fiber, and the process for which the coat material which contains a colloid oxide as a principal component is prepared, (c) Apply this coat material to the peripheral face of said ceramic honeycomb body, and it is filled up with the concave which exists in the peripheral face of this ceramic honeycomb body. The technique characterized by including the process which forms the outer shell layer of predetermined thickness, and the process which makes the outer shell layer formed in the peripheral face of (d) this ceramic honeycomb body dry or calcinate, and makes this ceramic honeycomb object fix this outer shell layer is adopted.
[0013] Furthermore, the coat material used in order that this invention may form the outer shell layer in the ceramic honeycomb structure object like **** Having constituted so that a cordierite particle and/or ceramic fiber, and a colloid oxide might be included as a principal component If it considers as the description and is in such coat material Colloidal silica or a colloidal alumina is used for a colloid oxide, and it is made for it to be advantageously blended with it at a rate of 3 - 35 weight section by solid content conversion to the 100 weight sections of a cordierite particle and/or ceramic fiber.
[0014]
[A concrete configuration and an operation] Although the ceramic honeycomb body which gives the ceramic honeycomb structure object according to this this invention in here is manufactured through each process of extrusion molding, desiccation, and baking using a cordierite system ceramic ingredient, usually As stated previously, the thin thing and the large-sized thing of thickness of a rib (septum) which divide a cel mutually Without also producing any defect, it is difficult to form an outer wall in one, and cel deformation of the periphery section and cel **** arise on the honeycomb body acquired, or the crack has arisen in the outer wall (peripheral face). As shown in drawing 1 and drawing 2 , namely, the honeycomb object 2 formed in one of extrusion molding using a cordierite system ceramic ingredient Although it has the through tube 6 of a large number surrounded by the septum 4, and the cel (6) mutually divided with the septum 4 in shaft orientations according to the application made into the purpose if it puts in another way so that the cel of predetermined magnitude may be given The septum 4 of the periphery section deformed, and cel ****** 8 has occurred, and the crack 10 has occurred in the outer wall.
[0015] By the way, although a wire mesh will be twisted around the periphery section, the three way catalytic converter and DPF using a ceramic honeycomb structure object will usually be stored in casing and it will be carried in an automobile If it is when the honeycomb object 2 which cel ****** 8 like **** and a crack 10 generated is used as a ceramic honeycomb structure object, the honeycomb object 2 is destroyed within casing in the compressive force by periphery grasping, and it becomes impossible to completely expect the operation as a catalytic converter or a filter. For this reason, although reinforcement is needed for the honeycomb object 2, even if it performs periphery reinforcement in the condition [that cel defects and cracks, such as cel ****, have gone into the periphery section of the conventional cure 2 against **** reinforcement, i.e., a honeycomb object,],

the destruction at the time of hold into the above-mentioned casing comes to be caused by the part where the mechanical strength of the honeycomb object 2 is the weakest. It **, and in the honeycomb object 2 reinforced as mentioned above, although the rise on the strength is achieved by reinforcing materials, since it does not succeed in reinforcement, the periphery section comes to be destroyed in this cel ****** by cel ****** whose mechanical strength of the honeycomb object 2 is the weakest part. In short, in the condition that cel ****** exists, even if it performs the periphery reinforcement to the honeycomb object 2, effectiveness must have been discovered effectively.
[0016] Although such a phenomenon is corresponding only to the honeycomb object 2 with cel ******, if rib thickness becomes thin, even if the mechanical strength (represented by periphery grasping on-the-strength slack AISO static reinforcement) does not have cel **** in the periphery section of the metaphor honeycomb object 2, it is very weak and periphery reinforcement is needed. Inevitably, if periphery reinforcement is carried out **(ing) and leaving the honeycomb outer wall section, since it will increase and the difference of rib thickness and outer wall thickness becomes large, the stress generated at the time of expansion by the exhaust gas temperature at the time of real use and the catalyst printing temperature in a catalyst support process and contraction will increase, and a crack will become easy to generate honeycomb outer wall thickness (degradation of thermal shock resistance). Moreover, since there is little adhesion area between the reinforcement layers and honeycomb objects which are formed of coat material even if it carries out periphery reinforcement, with such an outer wall left, coat exfoliation is caused and it is inherent in the problem which cannot demonstrate the periphery reinforcement effectiveness advantageously.
[0017] For this reason, if it is in this invention, the ceramic honeycomb body which does not have the outer wall section formed in one as a honeycomb object which gives a ceramic honeycomb structure object, i.e., the honeycomb body which has the concave formed by the septum with which it divides between cels in shaft orientations, is used. That is, as shown in drawing 3 , the ceramic honeycomb body 14 which forms the concave 12 to which what is located in the outermost part of the periphery section among the cels 6 of a large number mutually divided with the septum 4 prolonged in shaft orientations carries out opening outside, and extends in shaft orientations by not having a septum between the exteriors will be used. the honeycomb body 14 which has a concave according to such this invention carries out grinding of the periphery section of the honeycomb object 2 which has in one the peripheral wall produced by the conventional extrusion-molding technique described previously until cel **** is lost -- or it can obtain easily by fabricating so that the periphery configuration shown in drawing 3 may be given etc., without forming the outer wall section at the time of extrusion molding. If an outer wall is not formed at the time of this extrusion molding, since balance adjustment of the extrusion speed at the time of shaping serves as only the comparatively uniform honeycomb section, it can control or prevent generating of cel **** in the periphery section from the place which can disregard the extrusion speed of the outer wall section from which the amount of supply of a raw material plastic matter differs at the time of shaping effectively.
[0018] Thus, the ceramic honeycomb body 14 used in this invention By the grinding of the periphery section, or control of shaping actuation, from the place when cel ****** will not exist in the periphery section It becomes what does not have the weakest part of the mechanical strength of a honeycomb structure object, and, so, improvement in effective AISO static reinforcement can be aimed at by performing the below-mentioned periphery reinforcement to the honeycomb body 14 of such a condition.
[0019] And this invention is used as the ceramic honeycomb structure object by which was filled up by the periphery reinforcing materials of the periphery section represented by coat material in a concave 12 at least, and was made to form the outer shell layer of the predetermined thickness which gives an outside surface, with periphery reinforcement was carried out and which is made into the purpose to the ceramic honeycomb body 14 which has the concave prolonged in such shaft orientations in a peripheral face. Namely, as predetermined coat material is made to apply, with it is shown in drawing 4 and drawing 5 to the periphery section of the honeycomb body 14 shown in drawing 3 It is the thing is filled up with the inside of the concave 12 punctured in the periphery section at least, forms the outer wall section slack outer shell layer (coat layer) 16 which gives an outside surface, and it is made to serve as a predetermined dimension and cylindricity. By this

Improvement in the effective AISO static reinforcement of the ceramic honeycomb structure object 18 acquired can be attained.

[0020] Moreover, if it is in the ceramic honeycomb structure object 18 acquired by doing in this way, by forming the concave 12 in the periphery section of the honeycomb body 14, the adhesion area of the outer shell layer (coat layer) 16 and the honeycomb body 14 becomes large, and can also control or prevent effectively the exfoliation from the honeycomb body 14 of the outer shell layer 16. And from the place which does not have the honeycomb outer wall formed in one, the honeycomb body 14 is compared, when forming a reinforcement layer on the conventional honeycomb outer wall. Securing comparable mechanical strength, if it puts in another way in the thickness of the outer shell layer 16, outer wall thickness can be made thin. Being able to make small the difference of a honeycomb septum and outer wall thickness, it is mitigated by this and the thermal stress between an outer wall (outer shell layer 16) and the honeycomb body 14 serves as the honeycomb structure object 18 strong against a thermal shock by it.

[0021] Furthermore, although the thermal expansion and heat shrink generally become larger than the honeycomb body 14 about the coat material of periphery reinforcing materials slack various kinds applied to this honeycomb body 14, the effectiveness that the septum 6 which forms the concave 12 of this honeycomb body 14, i.e., a cel, and the septum 4 with which it divides between six ease them is shown, and the stress generated in the outer wall (16) formed in such coat material is decreased. And according to these phenomena, it is filled up with the concave 12 of the honeycomb body 14 which has the concave 12 formed by the septum 4, and the honeycomb structure object 18 in which the outer shell layer 16 which gives an outside surface was formed can hold sufficient reinforcement to be carried in an automobile, and can demonstrate sufficient thermal shock resistance under high dependability under the operating environment.

[0022] In addition, in the writing **** ceramic honeycomb structure object 18, generally, although the coat layer slack outer shell layer 16 which constitutes the peripheral wall is formed from the inorganic binder which combines the aggregate and it Especially as the aggregate, a coefficient of thermal expansion is small, and the cordierite (baking powder) of the shape of a particle without change of the crystal phase by the heat history shall be used advantageously, and the outer shell layer 14 shall have the main crystal phase which consists of cordierite by it. The reason nil why cordierite is desirable as this aggregate is as follows. Namely, although thermal stress occurs to each part at the time of heating of a honeycomb structure object and cooling and it comes to concentrate such thermal stress on the interface of a honeycomb body and an outer shell layer When the time when the thermal expansion of an outer shell layer and a honeycomb body is the same serves as min and there is a differential thermal expansion of an outer shell layer and a honeycomb body, this thermal stress In order that it may be eased effectively and problems, such as generating of the crack in the outer shell layer (peripheral wall) according [the one where the thermal expansion of an outer shell layer is smaller] to such thermal stress, may reduce the thermal expansion of an outer shell layer for this reason Cordierite with a thermal expansion smaller effectively [reducing the thermal expansion of the aggregate] therefore than the matrix given with the inorganic big binder of thermal expansion may be advantageously used as the aggregate. By this Thermal expansion of an outer shell layer is made small, and can consider as the honeycomb structure object strong against thermal stress.

[0023] In addition, although the cordierite used as this aggregate is generally baking powder which has the mean particle diameter of 50 micrometers or less, the thing and mean particle diameter of 15 micrometers or less will be advantageously used [mixture with a thing 30 micrometers or more etc.] for a thing with two steps of particle size distributions which consist of blends with a thing with mean particle diameter detailed especially, and a thing with comparatively coarse mean particle diameter, for example, mean particle diameter. Moreover, by replacing with such a cordierite particle and using as the aggregate, the ceramic fiber which consists of an amorphous mullite or an amorphous silica alumina as the part, generating of the crack of an outer shell layer is prevented advantageously, and there is an advantage to which you may make it contribute to control of the exfoliation etc. effectively. In addition, as this ceramic fiber, fiber length:10-15micrometer and an about [diameter:of fiber2-3micrometer] thing will be used advantageously.

[0024] Moreover, generally the matrix given with the inorganic binder which combines the aggregates, such as a writing **** cordierite particle and ceramic fiber, and forms an outer shell

layer is an amorphous oxide matrix, and it is advantageously formed by using colloidal silica or a colloidal alumina as an inorganic binder. In this invention, although it is also possible to use inorganic binders, such as well-known water glass and alumina cement, from the former, by using colloidal silica or a colloidal alumina as an inorganic binder especially, the heat-resistant property of the outer shell layer 16 as a peripheral wall formed in the periphery section of the honeycomb body 14 is raised advantageously, and an improvement of the heat-resistant impact property of the honeycomb structure object 16 acquired can be attained advantageously.

[0025] In addition, if it is when using the colloid oxide like this colloidal silica and colloidal alumina as an inorganic binder, as for such colloid oxide, it is desirable that you are made to blend at a rate of 3 - 35 weight section by solid content conversion to the 100 weight sections of a cordierite particle and/or ceramic fiber. the reinforcement of an outer shell layer -- securing -- the aggregate -- if it is because it is necessary to use it, being [more than 3 weight sections] comparatively alike at least, and setting and the operating rate increases too much, in order to make a cordierite particle and ceramic fiber fully fix -- the heat characteristic of an outer shell layer -- it is because the heat characteristic of the honeycomb structure object itself comes to get worse further.

[0026] By the way, manufacture of the ceramic honeycomb structure object according to writing **** this invention is faced. Although the coat material which contains the above-mentioned cordierite particle and/or ceramic fiber, and a colloid oxide as a principal component will be used advantageously and the periphery wall slack outer shell layer of a honeycomb body will be formed in this coat material An assistant with still more proper viscosity controlling agents, such as an organic binder, etc. may be made to blend with such coat material in consideration of the workability of covering to the honeycomb body of that if needed. And although such coat material will be applied to the peripheral face of the **** honeycomb body 14 shown in drawing 3 which has a concave according to this invention prepared separately in a peripheral face, it will be filled up with the concave 12 which exists in this peripheral face and the outer shell layer 16 of predetermined thickness will be formed Spreading to the peripheral face of the honeycomb body 14 of such coat material is faced. Various kinds of well-known applying methods will be adopted suitably, for example, a brushing method, a dipping method and the spray coating method that the viscosity of coat material is reduced and performs it, the coat method by casting, etc. will be adopted suitably.

[0027] Subsequently, according to the class of use coat material, required desiccation actuation or baking actuation is performed to the outer shell layer 16 as a peripheral wall formed in the peripheral face of the honeycomb body 14 in this way, and this outer shell layer 16 is made to be made to fix on the ceramic honeycomb body 14 by this. In addition, it is possible to calcinate the honeycomb body 14 to baking actuation and coincidence of this outer shell layer 16.

[0028] The ceramic honeycomb structure object 18 according to this invention obtained in this way As shown in drawing 4 and drawing 5 , the concave 12 of the shaft orientations prepared in the peripheral face of the ceramic honeycomb body 14 is filled up with coat material at least. While having the outer shell layer (coat layer) 16 as a peripheral wall which gives an outside surface and fully having the practical target reinforcement It excels also in thermal resistance or a heat-resistant impact property. Especially advantageously AISO static reinforcement is 3kg/cm2. Although thermal shock resistance is manufactured above as that in which 700 degrees C or more and the generating temperature of a crack have the property which is 800 degrees C or more and it may be advantageously used as catalyst support for emission gas purification etc. Moreover, also as DPF, a rotation accumulation type heat exchange object, etc. using a honeycomb structure object, it will be used suitably.

[0029]

[Example] It is a place needless to say that this invention is not what also receives any constraint by the publication of such an example although some examples of this invention are shown below and this invention is clarified still more concretely. Moreover, it should be understood that it is what can add modification which becomes various based on this contractor's knowledge, correction, amelioration, etc. to this invention unless it deviates from the meaning of this invention besides the following examples besides the further above-mentioned concrete description.

[0030] Example The plurality of the nature honeycomb object of cordierite with which it comes to fabricate a peripheral wall (rib thickness:150micrometer, cel consistency:62 cel / cm2, outer-

diameter dimension:300mm, and overall-length:300mm) in one as a ceramic honeycomb body with which one trial is presented was prepared. In addition, these cordierite honeycomb object has the cel **** part (8) in the periphery section, as shown in drawing 1 and drawing 2 . in addition, this honeycomb -- cel ****** (8) in the inside of the body is inevitably produced from crushing by that self-weight, when the outer-diameter dimension of a honeycomb object becomes large with 300mm. Moreover, rib thickness:150micrometer, the cel consistency 62 by which it comes to fabricate an outer wall in one : A cel / cm2, Outer-diameter dimension : The plurality of the nature honeycomb object of cordierite which has a cel **** part is used for the periphery section (310mm and overall-length:300mm). About each, grinding and the outer-diameter:300mm honeycomb object (refer to drawing 3) which removes and has a concave (12) in the periphery section were prepared for the cel **** part of the periphery section.

[0031] On the other hand, coat material was prepared in the presentation shown in the following table 2 using the raw material which has the material property shown in the following table 1, added and kneaded water further, and prepared it as a thing of various kinds of presentations in the shape of a paste which can be applied to a ceramic honeycomb object.

[0032]

[Table 1]

表 1

	平均粒子径*1 (μm)	固形分 (%)	化学組成（重量%）*2					
			MgO	Al_2O_3	SiO_2	CaO	Na_2O	ZrO_2
コージェライト粉末 A	20	—	13.7	35.5	50.6	0.1	0.2	—
コージェライト粉末 B	30	—	13.6	35.5	50.6	0.1	0.2	—
コージェライト粉末 C	10	—	13.7	35.4	50.5	0.1	0.2	—
珪酸ジルコニウム粉末	10	—	≦0.1	≦0.1	32.8	≦0.1	≦0.1	67.2
セラミックファイバー粉末A（非晶質ムライト）	10	—	≦0.1	72.0	28.0	≦0.1	≦0.1	—
セラミックファイバー粉末B（非晶質シリカーアルミナ）	10	—	≦0.1	48.0	52.0	≦0.1	≦0.1	—
無機バインダ A（水ガラス）	—	30	≦0.1	≦0.1	78.0	0.1	22.0	—
無機バインダ B（アルミナセメント）	—	100	0.4	73.2	0.8	25.4	0.2	—
無機バインダ C（コロイダルシリカ）	—	40	≦0.1	≦0.1	98.0	≦0.1	2.0	—
無機バインダ D（コロイダルアルミナ）	—	30	≦0.1	99.0	≦0.1	≦0.1	0.3	—

＊1 レーザー回折式粒度分析計による測定値
＊2 酸化物換算による測定値

[0033]

[Table 2]

表　　2

コート材 No.	コージェライト粉末A（重量部）	無機バインダ（重量部*1）		
		A	B	C
1	100	20	—	—
2	100	—	20	—
3	100	—	—	20
4	100	—	—	10
5	100	—	—	35

＊1　固形分換算での使用量

[0034] Subsequently, after applying the paste of various kinds of coat material shown in Table 2 to the periphery section of the honeycomb object (those with an outer wall) which do not have a concave in said prepared periphery section, and the honeycomb object (with no outer wall) which have a concave, respectively, it be left in atmospheric air for 24 hours, desiccation of 2 hours be performed at the temperature of 90 more degrees C, and various kinds of nature honeycomb structure objects of cordierite which come to give the periphery coat made into the purpose be acquired. In addition, the thickness of the periphery coat layer formed by doing in this way was about about 0.1-1mm. And in order to know the property of various kinds of nature honeycomb structure objects of cordierite acquired by giving this periphery coat, various kinds of performance tests were carried out. Moreover, the performance test with the same said of the nature honeycomb structure object of cordierite with which it does not have a concave and a periphery coat is not carried out by which the periphery section (rib thickness:150micrometer, cel consistency:62 cel / cm2, outer-diameter dimension:300mm, and overall-length:300mm) was fabricated in one for the comparison was carried out collectively. And the obtained result was shown in the following table 3.
[0035]
[Table 3]

表 3

ハニカム外壁状態	コート材No.	アイソスタティック強度 (Kg/cm²)	ハニカム熱衝撃強度 (℃)	クラック発生温度 (℃)	振動試験結果	剥離強度 (Kg/cm²)
コートなし（比較）	—	6．0	850	——	——	——
凹溝なし	1	8．8	≦350	≦300	剥離有り	1．9
	2	8．5	≦350	≦300	剥離有り	1．7
	3	10．2	700	800	剥離有り	2．0
	4	9．8	750	850	剥離有り	1．7
	5	11．5	600	700	剥離有り	3．5
凹溝あり	1	30．7	400	325	剥離なし	6．2
	2	27．6	400	350	剥離なし	6．0
	3	38．4	725	850	剥離なし	6．5
	4	36．7	800	900	剥離なし	5．0
	5	40．0	650	800	剥離なし	8．3

[0036] in addition, this table 3 -- setting -- an AISO static strength test -- the end face of the upper and lower sides of a honeycomb structure object -- thickness: -- it carried out by applying about 20mm aluminum plate, and wrapping and sealing a side face by the thickness:0.5mm urethane tube through about 0.5mm urethane sheet, putting into the pressurized container which filled water, raising a pressure gradually, and measuring a pressure when a noise of crack formation is made. In addition, the test sample offering number in this example was four pieces.

[0037] Moreover, the thin metal rod struck the peripheral wall of a honeycomb structure object lightly, putting a spalling test into the electric furnace which put the acquired honeycomb structure object on the frame which covered with the wire gauze, and was held at 700 degrees C, and having made it heat, and having taken out outside the furnace after 1 passage of time, and observing an appearance visually. It held outside the furnace for 1 hour until a crack was not discovered by appearance observation at this time, and the honeycomb structure object got cold in ordinary temperature, when a tap tone was a metallic sound, you put into the electric furnace further set as 25 degrees C or temperature high 50 degrees C rather than whenever [previous stoving temperature], and it was made to heat, and this actuation was repeatedly carried out until the honeycomb structure object broke. Destruction was considered as the time of discovering a crack or a tap tone turning into dulness, and impact strength was displayed by the maximum temperature by which a honeycomb structure object is not destroyed. In addition, in this trial, when a crack was not discovered by the periphery coat section at the time of destruction of a honeycomb structure object, said temperature up heating actuation was repeated and carried out, and that crack discovery temperature was displayed as crack initiation temperature until the crack was discovered by the periphery coat section. In addition, the number of test sample offerings in this example is three pieces, and the average is shown.

[0038] furthermore, peel strength -- periphery coat side:10mmx10mm from each honeycomb structure object, and a honeycomb -- the length -- the :30mm sample was started, the 30mmx30mmx10mm metal plate was pasted up on the periphery coat side and a honeycomb side, and it was shown in the result of having measured tensile strength. And the vibration test wound the wire mesh around the periphery of each honeycomb structure object, performed canning which holds

it in casing, they are acceleration:20G and vibration frequency:200Hz, was performed on the conditions of 100 hours, investigated the existence of exfoliation of a periphery coat, and showed it by the result again.

[0039] Cel ****** is in the periphery section, even if it gives a periphery coat to the honeycomb object which does not have the concave by which it comes to fabricate a peripheral wall in one, AISO static reinforcement not only does not improve substantially, but the fall of honeycomb thermal shock reinforcement is large, and the effectiveness of giving a periphery coat is not seen at all, so that clearly from the above result. However, if it is in some which gave the periphery coat to the honeycomb object which has a concave on a periphery without cel ******, AISO static reinforcement is made to improve effectively, it is the periphery coat section, and except for what a crack generates previously, compared with the honeycomb structure object using the honeycomb object with which the fall of honeycomb thermal shock reinforcement does not have a concave, either, it is few, and the crack initiation temperature of periphery coat material is also high. It is because it cannot succeed in the improvement and cannot succeed in a substantial improvement of AISO static reinforcement, even if the cel ****** is the weakest part and the reason gives a coat to a periphery in the honeycomb structure object containing cel ******, although a honeycomb structure object is destroyed in the weakest part about AISO static reinforcement. On the other hand, the honeycomb object which has a concave can lose cel ****** effectively, and effective reinforcement is realized when a coat is given to the periphery section.

[0040] Moreover, it is related to outer wall thickness and adhesion area that the fall of the honeycomb thermal shock reinforcement in the honeycomb structure object using the honeycomb object which does not have a concave and the crack initiation temperature of periphery coat material are low, from the place which gives a coat on the honeycomb section and the peripheral wall fabricated in one, the wall thickness of this peripheral wall increases and it is thought that it is for the tensile stress by the difference in contraction of a honeycomb object and a peripheral wall to increase. If it is in the honeycomb structure object acquired on the other hand using the honeycomb object which has a concave The stress by the peripheral wall which it comes to fabricate in one by a peripheral wall serving as only coat material From the place which is not what acts at all, the tensile stress of the peripheral wall formed by coat material comes to be absorbed as contraction stress by the honeycomb septum which forms a concave, and, for this reason, can control or mitigate the fall of honeycomb thermal shock reinforcement. Although the rise of AISO static reinforcement is considered when a periphery coat is given to the honeycomb object which such a phenomenon is fabricated by cel ****** not related in [the peripheral wall which does not have cel ****** temporarily] one, and does not have a concave The fall of honeycomb thermal shock reinforcement or crack initiation temperature still exists, and there are not a honeycomb structure object using the honeycomb object which does not have the concave by which the peripheral wall containing cel ****** was fabricated in one, and a substantial change.

[0041] Moreover, coat exfoliation is not caused [in / the peel strength of the periphery coat is high, and / a vibration test] if it is in the honeycomb structure object which comes to give a periphery coat to the honeycomb object which has a concave, although the honeycomb structure object using the honeycomb object which does not have a concave in the result of peel strength and a vibration test has low peel strength and coat exfoliation is caused also in a vibration test. The honeycomb object with which this has a concave with regards to the touch area of a honeycomb object and coat material has a large touch area with coat material compared with the honeycomb object which does not have a concave, and it is because fixing between coat material and a honeycomb object so becomes good.

[0042] It is clear to have the outstanding description which the honeycomb structure object which comes to fill up the concave of the peripheral face of a honeycomb object by coat material becomes the thing with high and AISO static reinforcement which also has high honeycomb thermal shock reinforcement compared with what carried out the coat to the honeycomb object which does not have a concave, and does not generate coat exfoliation at all, either from the above thing. In addition, since it is not realized as a product even if one of the properties of AISO static reinforcement and honeycomb thermal shock reinforcement deteriorate, The honeycomb structure object (honeycomb object) with which the periphery coat is not given As opposed to being that of which an AISO static

strength property is bad, and does not consist as a product If it is in the honeycomb structure object according to this invention which has a concave in a peripheral face, was filled up with it by coat material, and formed the peripheral wall, he combines and has the good property about AISO static reinforcement and honeycomb thermal shock reinforcement, and it is understood that it is what can fully be real-used.

[0043] example 2 -- in the presentation shown in following Table 4 - 7, it prepared using the raw material which has the material property shown in Table 1 of said example, and various kinds of coat material was adjusted in the shape of a paste which can be applied to the honeycomb object which adds and kneads water and is made into the purpose. Each coat material And rib thickness:76micrometer, and cel consistency:62 cel / cm2, Outer-diameter dimension : You make it apply to the nature honeycomb object 12 of **** cordierite shown in drawing 3 which has a concave on a periphery (100mm and overall-length:100mm). And after leaving it in atmospheric air for 24 hours, desiccation of 2 hours was performed at the temperature of 90 more degrees C, and the nature honeycomb structure object of cordierite which gave the periphery coat made into the purpose was acquired. And the AISO static reinforcement of this periphery coat honeycomb structure object of the obtained various kinds, honeycomb thermal shock reinforcement, and the crack initiation temperature of the periphery coat section were measured, and that result was shown in the following table 8.

[0044]

[Table 4]

表 4

コート材 No.	コージェライト粉末A（重量部）	無機バインダ（重量部*1）			
		A	B	C	D
1	100	20	—	—	—
2	100	—	20	—	—
3	100	—	—	20	—
6	100	—	—	—	20

＊1 固形分換算での使用量

[0045]

[Table 5]

表　5

コート材No.	珪酸ジルコニウム粉末（重量部）	無機バインダ（重量部*1）			
		A	B	C	D
7	100	20	—	—	—
8	100	—	20	—	—
9	100	—	—	20	—
10	100	—	—	—	20

＊1　固形分換算での使用量

[0046]
[Table 6]

表　6

コート材No.	コージェライト粉末（重量部）		無機バインダC（重量部*1）
	B	C	
11	100	—	20
12	—	100	20
13	50	50	20
14	50	50	2
15	50	50	5
16	50	50	35
17	50	50	50

＊1　固形分換算での使用量

[0047]
[Table 7]

表　7

コート材No.	コージェライト粉末A（重量部）	セラミックファイバー粉末　（重量部）		無機バインダC（重量部*1）
		A	B	
18	80	20	—	20
19	80	—	20	20
20	20	80	—	20
21	20	—	80	20
22	—	100	—	20
23	—	—	100	20

＊1　固形分換算での使用量

[0048]
[Table 8]

表 8

コート材 No.	アイソスタティック強度 (Kg/cm²)	ハニカム熱衝撃強度 (℃)	クラック発生温度 (℃)
コートなし	≦1．0	925	———
1	7．0	≦600	≦600
2	6．7	≦600	≦600
3	7．8	850	950
6	7．0	875	950
7	7．4	≦600	≦600
8	6．8	≦600	≦600
9	8．4	650	700
10	7．2	675	700
11	7．6	850	950
12	7．8	850	950
13	9．5	850	950
14	3．2	925	1100
15	4．3	925	1100
16	10．0	850	950
17	12．0	750	800
18	7．9	850	1000
19	7．8	825	1000
20	7．8	850	950
21	8．0	850	1000
22	7．8	825	950
23	8．0	850	1000

[0049] [when water glass and alumina cement are used as an inorganic binder so that clearly from the result of this table] If it is when the remarkable rise of AISO static reinforcement is accepted and colloidal silica and a colloidal alumina are used as an inorganic binder As an inorganic binder with which the very high value is acquired and honeycomb thermal shock reinforcement so also constitutes a periphery coat with AISO static reinforcement It is understood that the property of a honeycomb structure object of having given the periphery coat whose direction which used the colloid oxide like colloidal silica or a colloidal alumina is a final product rather than water glass or alumina cement is excellent.

[0050] Moreover, although AISO static reinforcement will become high a little rather than cordierite if the silicic acid zirconium powder currently used from the former is used as the aggregate of coat material, it is admitted that cordierite is excellent in the improvement effect of honeycomb thermal shock reinforcement or the crack initiation temperature of coat material. It is thought that the inclination based on the class of such the aggregate used is because the thermal expansion of cordierite is lower than the thermal expansion of a silicic acid zirconium. moreover, since the

inclination in AISO static reinforcement had the porosity of a silicic acid zirconium lower than the porosity of the cordierite used for this example and the inorganic binder acted effective in a silicic acid zirconium, it thinks -- having -- the porosity of cordierite -- a silicic acid zirconium and until comparable -- an equivalent value can be acquired if it is made low. If it puts in another way, when the porosity of the ingredient used as the aggregate is high, the lower one of the porosity of the aggregate with which an inorganic binder invades into an aggregate particle, stops being able to act easily effective in association between particles, and is so used, especially a cordierite particle is desirable.

[0051] Furthermore, about the cordierite powder used as the aggregate of a periphery coat, rather than a particle (mean particle diameter of 10 micrometers), coarse grain (mean particle diameter of 30 micrometers), or the thing that used only the middle particle (mean particle diameter of 20 micrometers), although both coarse grain and particle were mixed, it is admitted that the way can acquire a high value in AISO static reinforcement. Moreover, although AISO static reinforcement becomes high by increasing the amount of inorganic binders used as periphery coat material, the inclination for honeycomb thermal shock reinforcement to fall is accepted. Such a phenomenon becomes more precise [the packing condition of a particle] by using collectively the two or more aggregates with which particle size distributions differ, and when the effectiveness as a reinforcement wall of an outer shell layer increases, it appears. Moreover, the fall of the honeycomb thermal shock reinforcement by the increment in an inorganic binder Compared with the thermal expansion of the cordierite particle used as the aggregate, and a honeycomb body, the thermal expansion of the oxide matrix formed of desiccation of an inorganic binder is large. By a lot of inorganic binder addition Since the fixing force of the periphery section and the honeycomb section is reinforced, although AISO static reinforcement becomes strong, since the thermal stress of a honeycomb body and the periphery section increases, honeycomb thermal shock reinforcement comes to fall.

[0052] Furthermore, even if it uses ceramic fiber in addition to cordierite powder and this ceramic fiber permutes the whole quantity of cordierite powder, or its part as the aggregate again, while honeycomb thermal shock reinforcement comparable as the coat material which used only cordierite powder, and AISO static reinforcement are obtained, the inclination which the crack initiation temperature of coat material becomes higher, and shows the outstanding property is accepted.

[0053]

[Effect of the Invention] The ceramic honeycomb structure object according to this invention so that clearly from the above explanation The concave is filled up with coat material using the ceramic honeycomb body which has the concave prolonged in shaft orientations in a peripheral face. Attaining effective reinforcement of a honeycomb structure object from the place in which the outer shell layer which forms an outside surface is prepared The fall of the honeycomb thermal shock reinforcement which prevents a fall [honeycomb structure object in use / by exfoliation of the coat layer which is an outer shell layer] on the strength, and is caused in the case of reinforcement of a honeycomb structure object can be made to control effectively.

[0054] If it is in the ceramic honeycomb structure object according to this invention in short Exfoliation of the outer shell layer, generating of a crack, etc. are prevented effectively, the effective reinforcement being attained. Moreover, while making the thermal resistance improve, also being able to aim at effectively an improvement of the thermal shock resistance of a honeycomb structure object further and succeeding that it is easy in manufacture of such a characteristic honeycomb structure object A predetermined outer-diameter dimension and predetermined cylindricity may be made to realize advantageously, the dimensional accuracy can be raised effectively, and it may be adapted in favor of exhaust gas catalyst equipment, an exhaust gas purge, etc.

[0055] Moreover, the honeycomb structure object which gave the periphery coat used as a product can combine and have the outstanding AISO static reinforcement and honeycomb thermal shock reinforcement by using the aggregate and the inorganic binder according to this invention as coat material which gives the outer shell layer which forms the outside surface of such a honeycomb structure object.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the strabism explanatory view showing the cel **** defect of the periphery section of an extrusion-molding honeycomb object.
[Drawing 2] It is the partial expansion explanatory view of the cel **** defective part in drawing 1 .
[Drawing 3] It is the expansion explanatory view of the periphery section showing an example of the ceramic honeycomb body used in this invention.
[Drawing 4] It is the explanatory view corresponding to drawing 3 showing the condition that the coat layer was formed in the periphery section of the ceramic honeycomb body shown in drawing 3 , and the outer shell layer was prepared.
[Drawing 5] The concave of the peripheral face of the ceramic honeycomb body shown in drawing 3 is the strabism explanatory view showing an example of a ceramic honeycomb structure object according to this invention which it comes to fill up with coat material.
[Description of Notations]
2 Ceramic Honeycomb Object
4 Septum
6 Cel
8 Cel ******
10 Crack
12 Concave
14 Ceramic Honeycomb Body
16 Outer Shell Layer
18 Ceramic Honeycomb Structure Object

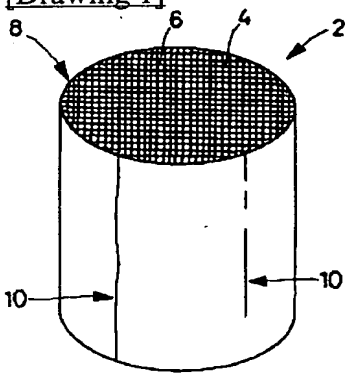
[Translation done.]

* NOTICES *

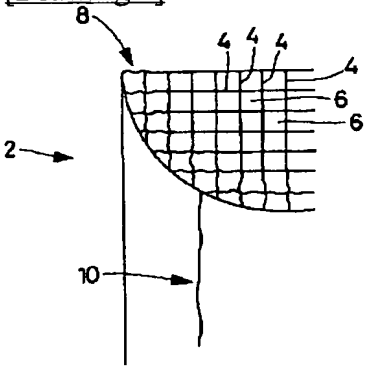
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

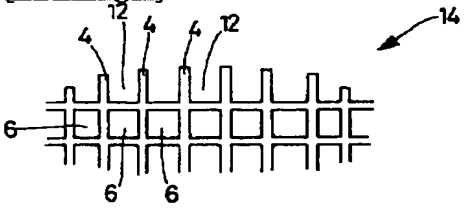
[Drawing 1]



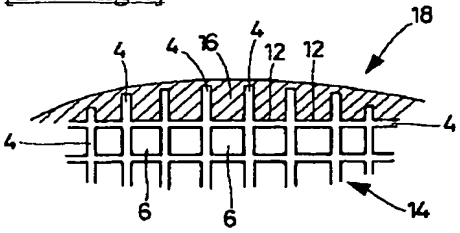
[Drawing 2]



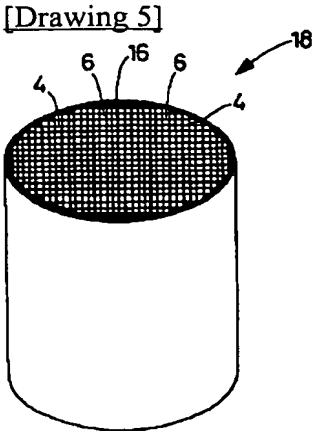
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]